UNIVERSITY OF MALTA

THE MATRICULATION CERTIFICATE EXAMINATION
ADVANCED LEVEL

CHEMISTRY
May 2012

MARKING SCHEME

MATRICULATION AND SECONDARY EDUCATION
CERTIFICATE EXAMINATIONS BOARD

Paper 1

1. (a) Elements in the s-block form a variety of ionic compounds. Define the term *ionic bond*.

(2 marks)

Is the electrostatic attraction (1)

Between oppositely charged ions (1)

(b) The statements given below refer to crystalline sodium chloride. Read each statement and decide whether it is *True* or *False*. Give a reason for each answer.

(i) In a sodium chloride crystal, each sodium ion is only bonded to the chloride ion it donated its electron to.

False (½)

A Na$^+$ ion is bonded to each of the neighboring negative Cl$^-$ ions (1)

(ii) A sodium atom can only form one ionic bond, because it has one electron in its outer shell to donate.

False (½)

A Na$^+$ ion can bond to as many Cl$^-$ ions that can arrange themselves around it i.e. 6. (1)

(3 marks)

(c) Place the ions Li$^+$, Na$^+$ and Cs$^+$ in the order indicated, giving a reason for each answer:

(i) increasing ionic radius;

Li$^+$ Na$^+$ Cs$^+$ (1)

Ionic radius increases due to increase in shielding which outweighs the increase in nuclear charge and increase in number of occupied electron shells resulting in a larger radius (½ ½)

(ii) increasing polarizing power;

Cs$^+$ Na$^+$ Li$^+$ (1)

The charge to radius ratio increase from Cs$^+$ to Na$^+$ to Li$^+$ hence polarizing power increases. (½ ½)

(iii) increase in covalent character of the iodide.

Cs$^+$ Na$^+$ Li$^+$ (1)

Li$^+$ is the cation with the greatest polarizing power, it will polarize the anion (I$^-$) more than the other cations and the bond will have greater covalent character (½) (½)

(6 marks)(Total: 11 marks)

2. (a) On vaporization, 0.150 g of a red volatile liquid displaced a volume of 30.0 cm^3 measured at 100 °C and 100 kPa. Find the molar mass of the red liquid.

(3 marks)

$PV = nRT = (m/M)RT$ **(1)**

$M = mRT/PV$

$= 0.15 \times 8.31 \times 373/100\,000 \times 30 \times 10^{-6} = 154.98$ (155) **(1 ½)**

Units = $g\ mol^{-1}$ **(½)**

(b) On combustion in excess oxygen, 0.200 g of the red liquid produced 0.0981 g chromium(III) oxide. Calculate the percentage by mass of chromium in the liquid.

(3 marks)

0.0981 g of Cr_2O_3 contains $[0.0981 \times 52 \times 2/(52\times2 + 16\times3)]$ g Cr =0.0671 g **(2)**

Hence % Cr in red liquid = 0.0671/0.2 X 100 = 33.6 % (1)

(c) If the red liquid also contains 45.8 % chlorine and the rest is oxygen, determine its empirical and molecular formula.

(3 marks)

% oxygen in red liquid = 100 – (45.8 + 33.6) = 20.6

Hence mol Cr : mol Cl : mol O = 33.6/52 : 45.8/35.5 : 20.6/16

= 0.646 : 1.29 : 1.29 = 1 : 1.99 : 1.99 = 1:2:2 (1 1/2)

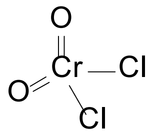
Hence empirical formula = CrO_2Cl_2 (1/2)

Formula mass = 52 + (16 X 2) + (35.5 X 2) = 155 which is the same as the molar mass determined in (a) and hence molecular formula is also CrO_2Cl_2 (1/2, 1/2)

(d) Draw a likely molecular structure for the red liquid and explain whether it would be expected to exhibit optical isomerism.

(2 marks)

The molecule is probably tetrahedral (AB_4):



(1)

The molecule has a plane of symmetry and is therefore not chiral (1/2) so that it will not exhibit optical isomerism. (1/2)

(Total 11 marks)

3. The rate of reaction of two substances **X** and **Y** was investigated by sampling the reaction mixture and titrating. The reaction taking place may be represented as:

$$\mathbf{X}\,(aq) + \mathbf{Y}\,(aq) \xrightarrow{\text{acid catalyst}} \mathbf{Z}\,(aq) + \mathbf{Q}\,(aq)$$

The procedure is repeated changing the concentration of each substance in turn. The results obtained are shown in the table.

Experiment	***Initial concentrations/ mol dm^{-3}***			***initial rate / mol dm^{-3} s^{-1}***
	[Y]	***[X]***	***[HCl (aq)]***	
I	0.001	0.5	1.25	1.1
II	0.002	0.5	1.25	1.1
III	0.002	1.0	1.25	2.2
IV	0.002	1.0	2.50	4.4

(a) Why is the procedure repeated *changing the concentration of each substance in turn*?

In order to determine how the rate changes when only one variable (one reactant concentration) is changed. (1)

(b) Find:

(i) the order of reaction with respect to **Y**;

Keeping concentrations of **X** and HCl constant:

Rate I/ Rate II = $(0.001/0.002)^n$ = 1.1/1.1 (1/2)

so n = 0. The reaction is zero order with respect to **Y**. (1/2)

(ii) the order of reaction with respect to **X**;

Keeping concentrations of **Y** and HCl constant:

Rate II/Rate III = $(0.5/1.0)^n$ =1.1/2.2 (½)

so n=1. The reaction is first order with respect to **X**. (½)

*(iii)*the order of reaction with respect to hydrochloric acid;

Keeping concentrations of **Y** and **X** constant to find the order of reaction with respect to HCl: (1/2)

Rate III/Rate IV = $(1.25/2.5)^n = 2.2/4.4$

so $n = 1$. The reaction is first order with respect to H^+ concentration. (1/2)

(c) *(i)* Define *overall order* of a reaction.

Overall order = sum of individual order with respect to reactants (½)

(ii) Find the overall order of the reaction between **X** and **Y** in the presence of acid catalyst.

The reaction is second order over all. (½)

(d) Write the rate equation for this reaction and find the value of the rate constant, stating its units.

(3 marks)

Rate = k [X(aq)][HCl(aq)] (1)

Considering Experiment I: 1.1 = k x 0.5 x 1.25
k= 1.76 mol^{-1} dm^3 s^{-1}
OR
Considering Experiment II: 1.1 = k x 0.5 x 1.25
k= 1.76 mol^{-1} dm^3 s^{-1}
OR
Considering Experiment I: 2.2 = k x 1.0 x 1.25
k= 1.76 mol^{-1} dm^3 s^{-1}
OR
Considering Experiment I: 4.4 = k x 1.0 x 2.50
k= 1.76 mol^{-1} dm^3 s^{-1}

(1 mark for calculation)
(½ mark for ans)
(½ mark for units)

(e) Explain what the results of this experiment imply with regards to the likely mechanism of this reaction.

(3 marks)

Y must be present for the reaction to occur, (½)
but its concentration does not appear in the rate equation. (½)
The reaction takes place in steps. (½)

The rate of the reaction cannot be faster than the rate of the slowest step and In the rate equation only the step which is rate-determining is represented. (½, ½)

In this reaction, Y is involved in a fast non-rate determining step, and only X and HCl, which appear in the rate equation are involved in the rate-determining step of the reaction which involves a bimolecular collision between these two species. (½)

4. Osmium (symbol Os) is a d-block element with electronic configuration **[Xe]$4f^{14}5d^{6}6s^{2}$** .

(a) Why can Os be classified as a d-block element?

Its last electron goes in a d-orbital (1)

(b) Os^{3+} is expected to be a stable oxidation state while Os^{2+} is expected to be a reducing agent. Explain this statement with reference to the electronic configurations of these ions.

Os^{3+} [Xe]$4f^{14}5d^{5}$ has a <u>half-filled d-subshell</u> (d^5) which is <u>associated with a greater stability</u> (½, ½) (½)

Os^{2+} [Xe]$4f^{14}5d^{6}$ is <u>expected to be a reducing agent</u>, <u>losing one electron and achieving the stability of a half-filled sub-shell.</u>

(½)

(c) Os and its compounds are used as catalysts.

(i) What is a catalyst?

A substance which alters the rate of chemical reaction by providing a (½)
different route from reactants to products involving a lower activation energy (½)

[Do NOT award any marks for definitions stating that a catalyst alters the rate of chemical reaction <u>without taking part</u>.]

(ii) Explain why compounds of d-block elements tend to have this property.

The <u>variable oxidation number</u> of these elements may enable them <u>to take part in a sequence of reactions and emerge unchanged in the end</u>. (1) (1)

[NB This is mainly true when transition metal compounds are acting as redox catalysts; when the elemental forms function as heterogeneous (surface) catalysts, the variable oxidation property is probably less important but students are unlikely to make this point.]

e) Osmium forms the compound with formula $K_2[OsCl_6]$.

(i) State the oxidation number of Os and explain the bonding present in this compound.

Oxidation number of Os is +4 (½)

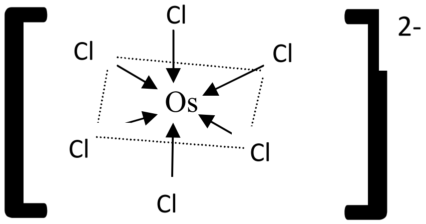
Bonding between K^+ and the complex anion is ionic (½)

In the complex anion, the bonding is

Ionic interaction between Os^{4+} and the Cl^- anions

(or dative covalent with six Cl^- donating an electron pair to Os^{4+}) (1)

(ii) Draw the structure of the anion in this compound.



(1) for shape
(½) for [ ]
(½) for charge

5. One mole of nitrogen gas was mixed with 3 moles of hydrogen gas and the reaction is allowed to reach equilibrium at 1000 K. The mole fraction of ammonia in the reaction mixture was 0.15 when the total pressure was 500 atm.

(a) Describe how the following factors change from the start of the experiment until equilibrium is reached:

(i) the rate of the forward and reverse reactions and

(ii) the partial pressures of nitrogen, hydrogen and ammonia.

(i) The rate of the forward reaction is relatively fast at the start but slows down as the concentration of reactants decreases. The rate of the reverse reaction is zero initially (as there is no ammonia) but starts to increase with time as the concentration of ammonia increases. At equilibrium the rate of the forward reaction is equal to the rate of the reverse reaction. (½) (½) (½) (½)

(II) The partial pressures of nitrogen and hydrogen decrease from the start of the reaction until equilibrium is achieved. The partial pressure of ammonia is (½)
zero initially and increases until equilibrium is reached. At equilibrium the (½)
partial pressure of each component remains the same. (½)
(½)

[Accept answers if given using properly labeled diagrams rather than in words.]

(b) Calculate the partial pressures of each component in the mixture.

$N_2 + 3H_2 \rightleftharpoons 2NH_3$
Initially 1 3 0
At eqm mole fraction NH_3 is 0.15
Therefore mole fraction of $N_2 + 3H_2$ is 0.85.
$N_2 + 3H_2$ were initially present in a ratio of 1:3 and reacted in a ratio of 1:3
Therefore at eqm they are still present in ratio of 1:3 (½)
Mole fraction N_2 is $\frac{1}{4} \times 0.85 = 0.212$
Mole fraction H_2 is $\frac{3}{4} \times 0.85 = 0.638$ (½)
(½)

pp $NH_3 = 0.15 \times 500 = 75$ atm
pp $H_2 = 0.638 \times 500 = 319$ atm (½)
pp $N_2 = 0.212 \times 500 = 106$ atm (½)
(½)

(c) Calculate a value for the equilibrium constant Kp for the reaction at 1000 K, stating its units.

$$Kp = \frac{pp^2\ NH_3}{pp\ N_2 \times pp^3\ H_2}$$ (1)

deduct ½ mark if square brackets are used

$$\frac{75^2}{319^3 \times 106}$$ (1)

$= 1.63 \times 10^{-6}$ (½)
Atm^{-2}. (½)

6. Fill in the blanks in the following table using any of the following chemical substances. Each property may fit one or more substances in which case include all correct answers in the table. Each substance may be used once or more than once or not at all.

$NaNO_3$, C_{60}, BaO_2, $CaCO_3$, BeO, $AlCl_3$, $SiCl_4$, PbO

Property	Chemical species

An allotrope of graphite.	C_{60}
A solid with important agricultural uses.	$NaNO_3$, $CaCO_3$
A white solid which releases an odourless colourless gas on heating.	BaO_2 , $NaNO_3$, $CaCO_3$
A white solid which produces a gas on treatment with dilute acid in the cold.	$CaCO_3$
A molecular liquid which reacts with water to give a white solid among the products.	$SiCl_4$
A solid which is insoluble in water but dissolves in both acid and alkali.	PbO, BeO
A solid which melts readily on heating to produce a molecular liquid which turns into vapour at higher temperature: the vapour dissociates reversibly on further heating.	$AlCl_3$
A non-conducting solid which reacts with hot concentrated nitric(V) acid to produce a mixture of gases and no solid residue.	C_{60}

Award 1 mark to each correct answer except for part (b) where each substance gets ½ mark (total 1); deduct 1 mark to each incorrect answer *to a minimum of 0 in each part*.

(11 marks)

7. This question is about the alcohol with the following structural formula.

$$CH_3CH(OH)(CH_2)_3CH_3$$

(a) Name and classify this alcohol as primary, secondary or tertiary and account for your answer.

(2 marks)

Hexan-2-ol (1)

Secondary alcohol because the OH group is linked to a secondary carbon atom which is one that is bonded to two carbons (½, ½)

(b) Explain why the alcohol is more soluble in diethyl ether than in water.

(1 mark)

Because the molecule has a prominent non-polar component of six methylene carbon atoms (½) which does not interact with polar water molecules (½)

(c) Explain why the alcohol exists in two optically active forms.

(1 mark)

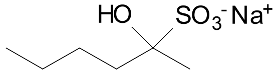
Because carbon-2 is dissymmetric (linked to four different groups) and the mirror Image forms are non-superimposable.

(d) On treatment with acidified dichromate, the alcohol produces a substance **R** which reacts with a solution of sodium hydrogensulfite to form a precipitate **P** Identify **R** and **P** and explain the reactions described.

(4 marks)

The oxidation product R is a ketone, hexan-2-one (accept structure instead of Name as identifier) (2)

With sodium hydrogensulfite, the addition compound is formed:

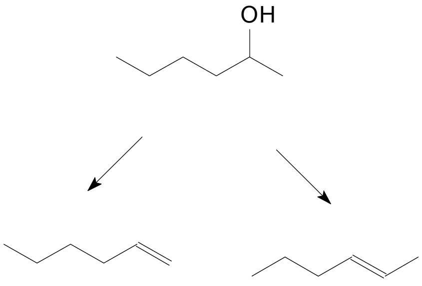


(2)

(e) On treatment with hot concentrated sulfuric acid, the alcohol produces a mixture of two structural isomers, **U** and **V.** The substance **U** is itself a mixture of two stereoisomers. Explain these observations, giving the structural formulae of all the isomers mentioned.

(4 marks)

Hot concentrated sulfuric acid acts as a dehydrating agent producing alkenes from alcohols (½). In this case, two alkenes can form thus:



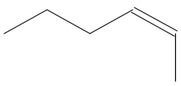
V

U

(1, 1)

But isomer U admits cis-trans (geometric) isomerism since it is an unsymmetrical alkene (½) thus:

Trans-

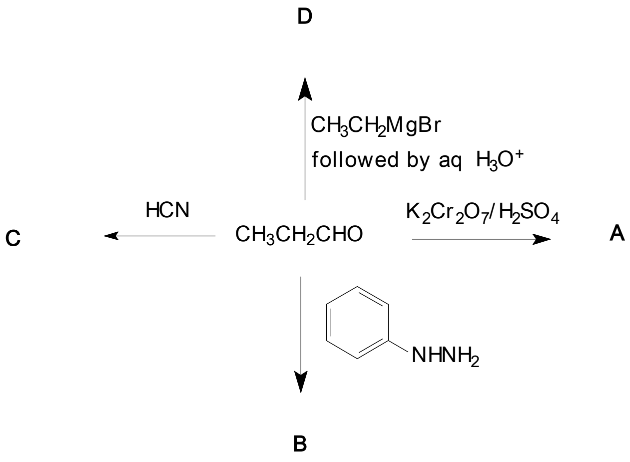


Cis-

(½, ½)

[Award 1 mark for the cis-trans isomer structures only if the answer clearly shows which isomer is which.]

8. Consider this reaction scheme involving propanal.



(a) Give structural formulae for substances **A, B, C** and **D**.

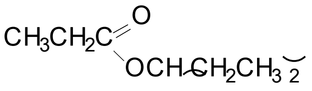
A = CH_3CH_2COOH (1)

B = $CH_3CH_2CH{=}N\text{-}NH(C_6H_5)$ (1 ½)

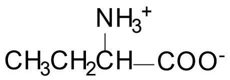
C = $CH_3CH_2CH(OH)CN$ (1 ½)

D = $(CH_3CH_2)_2CH(OH)$ (2) *(6 marks)*

(b) Explain how the following two substances **F** and **G** can be prepared using organic products from the reaction scheme in (a) and appropriate inorganic reagents.



F



$$CH_3CH_2\overset{NH_3^+}{\overset{|}{C}}H{-}COO^-$$

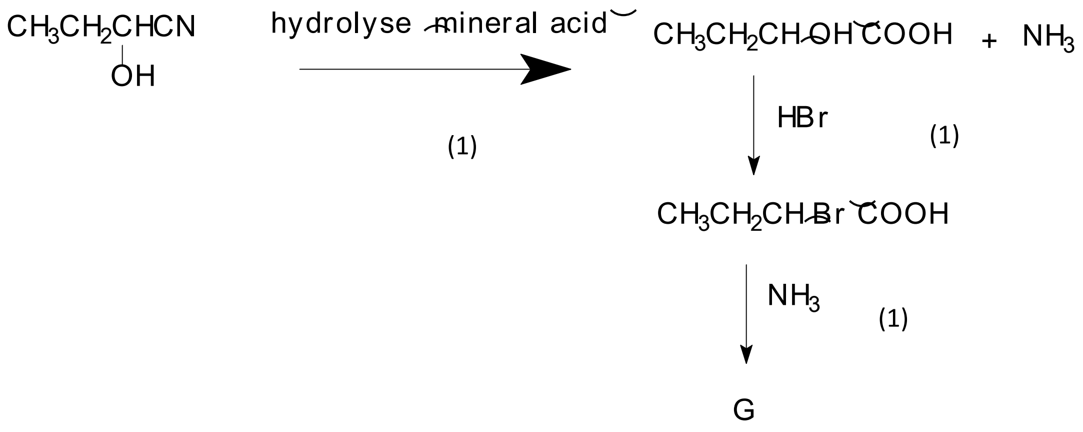
G

(6 marks)

F is an ester formed by reaction of the alcohol D and the carboxylic acid A. (1)

These two compounds are heated together in the presence of conc sulfuric acid as catalyst to form F. (Alternatively, the acid is first converted into the acid chloride (PCl_5) and then this reacts more completely with the alcohol to form F. **(1 ½)**

G is the dipolar (zwitterion) form of an amino acid **(½)** which can be obtained from compound C in the following manner:



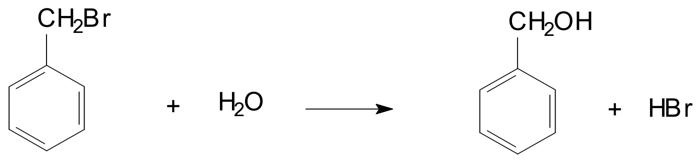
accept correct alternatives.

9. Explain the following observations as fully as you can, giving relevant chemical equations or structural formulae as appropriate.

(a) On adding drops of aqueous silver nitrate to liquid (bromomethyl)benzene in a test tube, a cream coloured precipitate forms; no precipitate forms if the organic liquid is 1-bromo-2-methylbenzene.

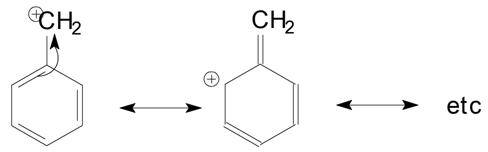
(3 marks)

The precipitate is AgBr (½) which forms due to presence of Br⁻ ion released from the ready hydrolysis of the bromomethyl group in side chain substituted arene:



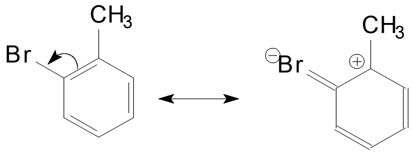
(½)

Reactivity due to formation of delocalized carbocation thus:



(1)

In the isomeric compound, no hydrolysis occurs since the C-Br bond is strengthened by delocalization (assumes partial double bond character) and is hence unreactive:

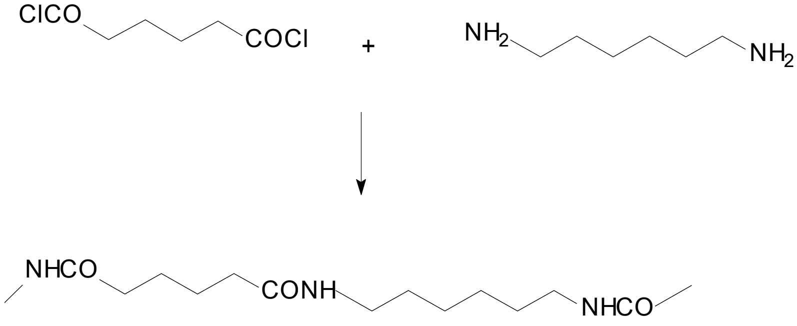


(1) fix

(b) When a solution of hexanedioyl dichloride ($ClOC(CH_2)_4COCl$) in hexane is added to an aqueous solution of hexane-1,6-diamine, a white solid forms at the interface of the two liquids from which a fibrous substance can be extracted and rolled onto a glass rod.

(3 marks)

At the interface between the two immiscible liquids, (½) a condensation polymerisation reaction occurs (½) forming Nylon/a fibrous polymer (½) due to reaction as follows:



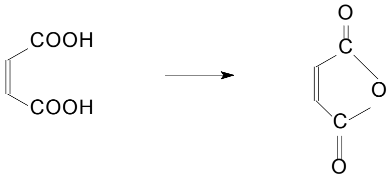
(1 ½)

(c) O

n gentle warming, crystals of *cis*-butenedioic acid produce a colourless liquid product which evaporates to leave a white residue; *trans*-butenedioic acid is stable to heat.

(3 marks)

The cis isomer dehydrates to form readily the anhydride since the two COOH groups are near each other and can eliminate water between them to form a stable ring structure (1)



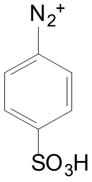
(1)

The geometry of the trans- isomer and the rigidity of the double bond act to prevent a similar chemical change. (1)

(d) When a solution of 4-aminobenzenesulfonic acid in dilute hydrochloric acid is added to an ice-cold solution of sodium nitrite, a colourless product is obtained; on adding this product to an alkaline solution of dimethylaminobenzene, an orange yellow precipitate forms.

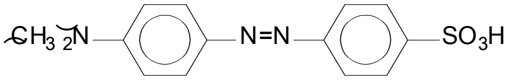
(3 marks)

Nitrous acid, HNO_2, forms when acid is added to nitrite (½) ; this acid diazotises the amino group in 4-aminobenzenesulfonic acid to form the colourless diazonium salt



(½)

Diazonium salt reacts with the dimethylaminobenzene, $N(CH_3)_2$-C_6H_5 (½) to form an orange yellow coloured azo dye (½) having the following structure:



(1)

Accept also as correct the ortho isomer. Do not penalize candidate if formation of a mixture of ortho and para isomers is not mentioned.

Paper 2

1. (a) A half cell made up of $Co^{3+}(aq)/Co^{2+}(aq)$ is connected to a half cell made up of $Br_2(aq)/Br^-(aq)$. The standard electrode potentials of the half cells at 25°C are:

$$Co^{3+}(aq) + e^- \longrightarrow Co^{2+}(aq) \qquad E^\theta = +1.82\ V$$

$$\tfrac{1}{2} Br_2(aq) + e^- \longrightarrow Br^-(aq) \qquad E^\theta = +1.07\ V$$

(i) Give a cell diagram for the reaction using the usual cell notation.

(ii) In which direction will electrons flow in the external circuit? Justify your answer.

(iii) Describe what, if anything, will happen to the colour intensity of the solution of the $Br_2(aq)/Br^-(aq)$ half cell.

(iv) Write a balanced ionic equation for the overall reaction.

(v) Calculate the E.M.F of the cell.

(vi) State, giving a reason in each case, which of the following: Br^-, Br_2, Co^{2+}, Co^{3+} is:

(I) the strongest oxidizing agent

(II) the strongest reducing agent. *(12 marks)*

(b) When a Cr^{3+}/Cr half cell is connected to an Fe^{3+}/Fe half cell, the Fe electrode is positive. When the Fe^{3+}/Fe half cell is connected to a Cu^+/Cu half cell, the Fe electrode is negative.

(i) Explain this observation.

(ii) Identify the weakest oxidizing agent among these two redox systems giving reasons for your answers.

(4 marks)

(c) Explain why magnesium alloys are used to protect the hulls of steel ships and other underwater structures from corrosion. *(4 marks)*

(a) (i) The cell diagram is

$Pt/2Br^-(aq), Br_2(aq) // Co^{3+}(aq), Co^{2+}(aq)/Pt$

1 mark for Pt electrode
1 salt bridge
½ for Br^-, Br_2 i.e. Reduced form, oxidized form
½ for Co^{3+}, Co^{2+} i.e. oxidized form, reduced form

Give full marks if cobalt half cell is drawn on the left. (3 marks total)

(a) (ii) The direction of electron flow is *from the bromine to the cobalt electrodes* because negatively charged particles are attracted by the positive pole of the cell. (½ ½)

(a) (iii) The red-brown colour will become more intense as more bromine molecules are formed. (1)

(a) (iv) Balanced ionic equation for the overall reaction:

$Co^{3+} + Br^{-} \rightarrow Co^{2+} + \frac{1}{2} Br_2$

½ reactants
½ products
1 for balancing

Accept if shown as $2\ Co^{3+} + 2\ Br^{-}$ etc.

(a) (v) Cell emf $= +1.82 - 1.07$ 1
$= +0.75V$ 1

(a) (vi)

Best oxidizing agent is <u>Co^{3+}</u> as it is <u>most ready to accept electrons</u> 1, ½
Best reducing agent is <u>Br^{-}</u> as it is <u>most ready to lose electrons</u> 1, ½

(12 marks)

(b) (i) From the statement: 1

Cr^{3+}/Cr half cell is connected to an Fe^{3+}/Fe half cell, the Fe electrode is positive

One can imply that the reduction of Fe^{3+} is favoured over the reduction of Cr^{3+} OR the Eo for the Cr^{3+}/Cr half cell is more negative OR Eo for the Fe^{3+}/Fe half cell is more positive.

Since it is given that

Fe^{3+}/Fe half cell is connected to a Cu^{+}/Cu half cell, the Fe electrode is negative 1

This implies that the reduction of Cu^{+} is favoured over the reduction of Fe^{3+}OR the Eo for the Fe^{3+}/Fe half cell is more negative OR Eo for the Cu^{+}/Cu half cell is more positive

(b) (ii) Hence, Cr^{3+} is a weaker oxidant (electron acceptor) than Fe^{3+} (½)

And Fe^{3+} is a weaker oxidant than Cu^{+} (½)
Hence <u>weakest oxidizing agent is Cr(III)</u> (and strongest is Cu(I))
(or Cu(I)>Fe(III)>Cr(III)) (1)

(4 marks)

(4 marks)

(c) Magnesium alloys are used as <u>sacrificial anodes</u> 1
When connected to a <u>weaker reducing agent</u> (**less reactive metal**), the magnesium ½ ½

becomes the anode of an electrical cell/donates electrons in the electrical cell to the other electrode (Fe(II)/Fe)

Mg corrodes in preference to the other metal ½
Iron (in steel) is a weaker reducing agent (less reactive) than magnesium (or Fe is lower in e.c.s) and hence ½
$Mg \Rightarrow Mg^{2+} + 2e^-$ in preference to $Fe \Rightarrow Fe^{2+}$ 1

2. Cyclohexene (C_6H_{10}) reacts with hydrogen giving cyclohexane (C_6H_{12}). The standard enthalpy changes of formation of cyclohexene and cyclohexane are -38.2 and -156 kJ mol^{-1} respectively.

(a) Define the term *standard enthalpy change of formation*. *(2 marks)*

(b) By drawing a suitable enthalpy change cycle, calculate the value of ΔH for the reaction:

$$\text{cyclohexene} + \text{hydrogen} \longrightarrow \text{cyclohexane}$$

(5 marks)

(c) Calculate a second value for ΔH for the reaction using the following average bond enthalpy terms (in kJ mol^{-1}) :

C-C 347, C-H 413, C=C 612 and H-H 436.

(5 marks)

(d) State which of your two answers is more accurate and explain why.

(2 marks)

(e) Why is it not correct to estimate the enthalpy of hydrogenation of benzene as three times the value obtained in (b) or (c)?

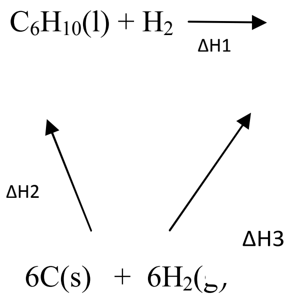
(2 marks)

(f) The enthalpy change of combustion of cyclohexane can be found experimentally and has a value of -3924 kJ mol^{-1}. On the other hand the enthalpy change of formation of cyclohexane cannot be measured directly. How can the enthalpy change of formation of cyclohexane be calculated using the value of the enthalpy change of combustion? What other quantities are required?

(4 marks)

(a) The standard enthalpy change of formation is the enthalpy change when 1 mole of a substance (1) is formed from its elements (½) in their standard states (½)

(b) Enthalpy change cycle:



1 mark for cycle including direction of arrow; 1 for balanced cycle;
deduct ½ if H used instead of H_2

(2)

According to Hess's Law

$\Delta H3 = \Delta H1 + \Delta H2$ (1)

$\Delta H3 - \Delta H2 = \Delta H1$

$-156 - (-38.2) = \Delta H1$ (1)

$-117.8 \text{ kJ mol}^{-1} = \Delta H1$ (1)

(c) Using the reaction:

Bonds broken		Bonds formed	
C=C = +612	1	C-C = -347	1
H-H = <u>+436</u>	1	2C-H = <u>-413x2</u>	1
+1048		-1173	

Enthalpy of hydrogenation = +1048 – 1173 = -125kJmol^{-1}. 1

Accept also:

Bonds broken		Bonds formed	
5C-C =	½	6C-C = -347x6	1
+347x5	½	12C-H = <u>-413x12</u>	1
10C-H = - 413x2	½	-7038	
C=C = +612	½		
H-H = <u>+436</u>			
+6913			

Enthalpy of hydrogenation = +6913 – 7038 = -125kJmol^{-1}. 1

(d) The answer to (c) is less accurate 1 as it is based on average values of bond enthalpies 1

(2 marks)

(e) The value of the enthalpy of hydrogenation of benzene will be **less** than three times the value obtained in (b) or (c) because benzene is **more stable** than the theoretical cyclohexatriene due to **delocalization** of electrons. ½ ½ 1

(f) Use the enthalpy change cycle:

$$\begin{tikzcd} C_6H_{12}(l) + 9O_2(g) \arrow[rr, "\Delta H2"'] & & 6CO_2(g) + 6H_2O(l) \\ & 6C(s) + 6H_2(g) + 9O_2(g) \arrow[ul, "\Delta H1"] \arrow[ur, "\Delta H3"'] & \end{tikzcd}$$

2 for cycle

1 for balancing

Using enthalpy of combustion of cyclohexane (given), **enthalpy of combustion of carbon and hydrogen are required.** 1

Accept also: enthalpy of formation of carbon dioxide and enthalpy of formation of water

Applying Hess's law ½

$\Delta H3 = \Delta H1 + \Delta H2$ ½

$\Delta H3 - \Delta H2 = \Delta H1$

$[(6\ \Delta Hc\ C) + (6\ \Delta Hc\ H_2)] - \Delta Hc$ cyclohexane

3. This question is about equilibrium processes.

(a) Hydrochloric acid of concentration $0.1 moldm^{-3}$ is used to titrate $40cm^3$ of ammonia solution, of concentration $0.05\ mol\ dm^{-3}$.

(i) Sketch a graph to show how the pH of the solution varies with the volume of acid added and on your graph indicate the range over which the solution is behaving as a buffer. In your answer, explain the meaning of *buffer* and how it works.

(ii) Three common acid-base indicators are:

Indicator	*pH range*
Thymol blue	1.2-2.8
Bromocresol green	3.8-5.4
Phenolphthalein	8.3-10.0

Which of these three indicators can be used to determine the end-point of the ammonia-hydrochloric acid titration? Explain why this indicator is the most suitable.

(8 marks)

(b) An aqueous solution of ammonia was shaken with a liquid silicone and the two layers were then allowed to separate (the liquid silicone acts as a solvent which is immiscible with water). On analysis, 20.0 cm^3 of the aqueous layer required 17.0 cm^3 of 1.00 mol dm^{-3} HCl for neutralization while 20.0 cm^3 of the silicone layer required 6.0 cm^3 of 0.0200 mol dm^{-3} HCl.

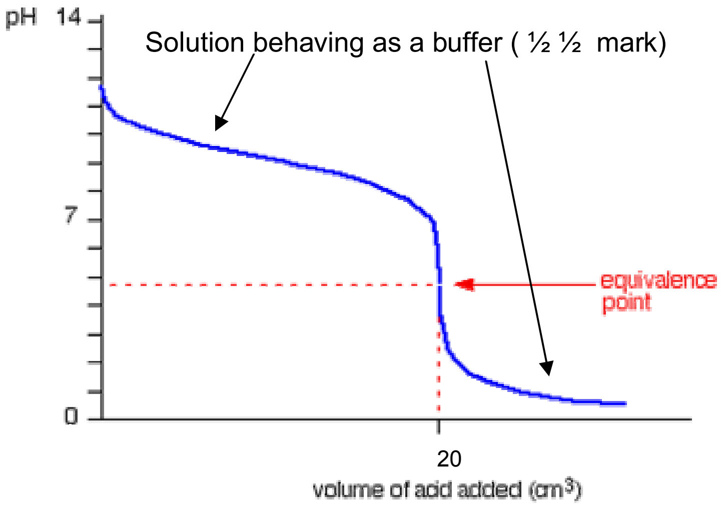
(i) Calculate the value of the partition constant of ammonia between water and the liquid silicone.

(ii) Explain how the principle behind this experiment may be used to extract and purify the product of a chemical reaction.

(8 marks)

(c) When bromobenzene is extracted by steam distillation at a pressure of 10^5 Pa, the mixture boils at 95.5°C. At that temperature the vapour pressure of pure water is 8.58 x 10^4 Pa. Calculate the percentage by mass of bromobenzene in the distillate. *(4 marks)*

(a) The graph is as follows:



- ½ starting pH around 11-12
- ½ rapid decrease of pH at start
- ½ slow decrease of pH after initial part
- ½ sharp drop in pH at the end point
- ½ pH at equivalence point less than 7 (around pH 5)
- ½ final pH around 1

fix

A buffer solution is one which will resist changes in pH on addition of small amounts of acid and alkali. 1

In this case the ammonia present and the ammonium chloride being formed in titration form the buffer hence the pH starts decreasing rapidly at the start but then decreases very slowly as more buffer solution is formed. 1

(ii) Best indicator: bromocresol green ½

It changes colour over the pH range 3.8-5.4

The pH at the equivalence point in this ½ why it is suitable

½ why phenolphthalein is not suitable

titration is less than 7 so phenolphthalein is not suitable. The pH range of thymol blue is below 7 but this is too low. ½ why thymol blue is not suitable

(8 marks)

(b) The partition equilibrium is written as follows:

$NH_3(aq) \rightleftharpoons NH_3(silicone)$

$\frac{[NH_3(silicone)]}{[NH_3(aq)]} = Kd$

To calculate $[NH_3(silicone)]$:

Moles of HCl used = $\frac{0.02 \times 6.0}{1000} = 1.2\times10^{-4}$ 1

Moles of $NH_3 = 1.2\times10^{-4}$

$[NH_3(silicone)] = \frac{1.2\times10^{-4} \times 1000}{20} = 6\times10^{-3} moldm^{-3}$ 1

To calculate $[NH_3(aq)]$:

Moles of HCl used = $\frac{1.00 \times 17.0}{1000} = 1.7\times10^{-2}$ 1

Moles of $NH_3 = 1.7\times10^{-2}$

$[NH_3(aq)] = \frac{1.7\times10^{-2} \times 1000}{20} = 0.85 moldm^{-3}$ 1

$Kd = \frac{6\times10^{-3}}{0.85} = 0.0072$ 1

Accept also:

$NH_3(silicone) \rightleftharpoons NH_3(aq)$

$\frac{[NH_3(aq)]}{[NH_3(silicone)]} = Kd$

$Kd = \frac{0.85}{6\times10^{-3}} = 141.67$

(ii) Aqueous solution of product is shaken with organic solvent in a separating funnel. 1
Product will distribute itself between the two layers according to the distribution coefficient. 1
Layers are separated ½
Procedure repeated to extract more solute ½

(c)

Vapour pressure at the boiling point, which equals the external atmospheric pressure, is the sum of the vapour pressures of Bromobenzene and water: ½

P(atmospheric) = 10^5 Pa = P(water) + P (bromobenzene) ½

Hence P(bromobenzene) = $10^5 - 8.58 \times 10^4 = 1.42 \times 10^4$

$$\frac{\text{Moles of bromobenzene in vapour}}{\text{Moles of water in vapour}} = \frac{\text{vp of bromobenzene}}{\text{vp of water}}$$ 1

$$= \frac{1.42\text{x}10^4}{8.58 \text{ x } 10^4} = 0.166$$ 1

$$= \frac{0.166}{1}$$

$$\frac{\text{Mass of bromobenzene}}{\text{Mass of water}} = \frac{0.166 \text{ x } 157}{1\text{x}18} = \frac{1.44}{1}$$

Percentage by mass of bromobenzene = $\frac{1.44}{2.44} \text{ x } 100 = 59.1\%$ 1

4. A compound **C** has the molecular formula C_3H_6ONBr. It reacts with phosphorus(V) oxide to produce compound **D** (C_3H_4NBr) and with aqueous alkali to form a product which on acidification converts into substance **E** ($C_3H_6O_3$). **E** reacts with thionyl chloride to form **F** ($C_3H_4OCl_2$) and with a mixture of iodine and aqueous sodium hydroxide to form a yellow precipitate **G** and a solution of **H** ($C_2O_4Na_2$) in water.

(a) Deduce the structural formulae of compounds **C, D, E, F, G** and **H** and explain the reactions described including relevant chemical equations. *(12 marks)*

(b) Compound **E** can be converted into the yellow liquid **I** having the following structure:

$$H{-}C{\equiv}C{-}COOH$$

(i) Name substance **I**.

(ii) Suggest a method for converting substance **E** into **I.**

(iii) Compound **I** has delocalized electrons. Draw canonical formulae to represent the delocalization in compound **I.** *(8 marks)*

(a) P_4O_{10} is a dehydrating agent and the **C** to **D** conversion involves loss of HOH from **C** which suggests C contains an amide group ($CONH_2$) (½). **D** is then a nitrile (½). Aqueous alkali would then hydrolyse the amide **C** to produce, after acidification, the parent acid, nitrogen being lost as ammonia. (½)

E is a carboxylic acid which reacts with $SOCl_2$ to introduce two not one chlorine atoms in F : hence E must be a hydroxyl acid (½) .

Moreover, reaction of E with iodine and alkali is the iodoform test (½) so that G is iodoform (½) and E must contain the $CH_3CH(OH)$- group (1): Thus probable structures are

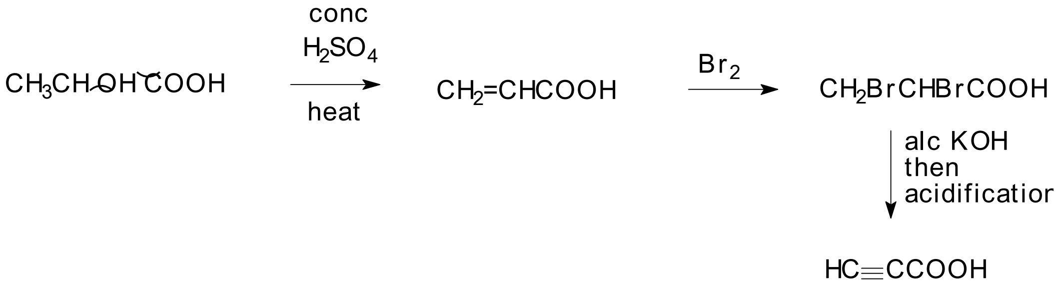
E = $CH_3CH(OH)COOH$; **(2)** H = $(Na^+)_2\,[COO\text{-}COO]^{2-}$ **(2)**

D = $CH_3CHBrCN$ **(1 ½)** C = $CH_3CHBrCONH_2$ **(1 ½)**

F = $CH_3CHClCOCl$ **(2)**

(b) (i) 2-propynoic acid. Accept also prop-2-ynoic acid and propynoic acid (1)

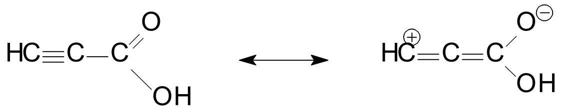
(ii)



Award for reagents/essential conditions: 1, 1, 1.

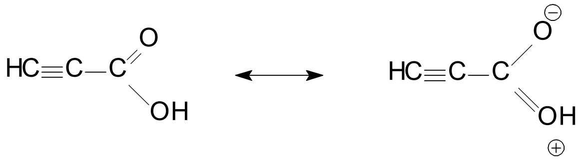
Award for correct intermediates: 1, 1.

(iii)



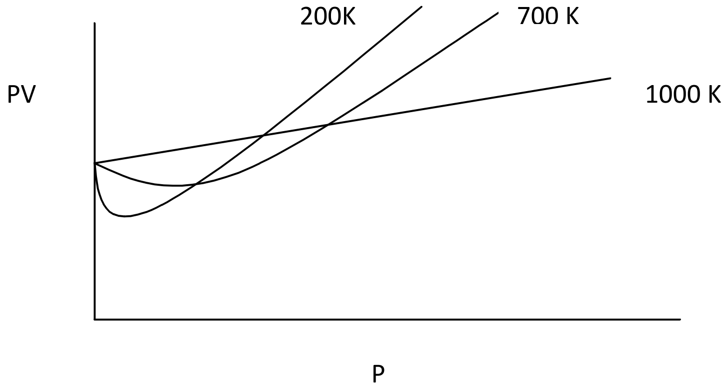
(2)

Award (1) if delocalization is shown involving only the carboxyl group (*not* the ionized carboxylate ion):



5. Explain ANY FOUR of the following observations. All parts carry equal marks.

(a) Graphs of PV *versus* P where P is the pressure and V is the volume of a fixed mass of nitrogen gas plotted at different temperatures are as shown in the diagram below.



This behaviour is not the same as that expected of an ideal gas.

(b) The relative molecular mass of ethanoic acid vapour changes with increasing temperature, from a value of about 120 at the lower to about 60 at the higher temperatures.

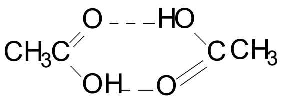
(c) Even though the molecules BF_3, NF_3 and ClF_3 have the same stoichiometry (XF_3), their molecular structure is different.

(d) The reaction of chlorine with ethene to form 1,2-dichloroethane involves formation of an intermediate carbocation; this explains why 2-chloroethan-1-ol is minor reaction product when the chlorination is performed in the presence of water.

(e) Knowing that the mass spectrum of a ketone contains, as main peaks, those with m/z values 29, 57 and 86 allows one to distinguish between pentan-2-one and pentan-3-one. *(20 marks)*

(a) Ideal gases obey relation $PV = nRT$ (1) which implies that PV is a constant at constant T and n (fixed mass) (1) so that the PV-P graph would be a horizontal straight line. (1) In the case of nitrogen, a real gas, increasing pressure affects the volume since molecules occupy space and have intermolecular forces of attraction. (1) At low temperatures, when the kinetic energy of the gas is reduced, the deviation due to intermolecular forces is greater (½) ; and at high pressures, when the volume is lower, the molecules collide more frequently and the forces of attraction are more important leading to greater deviation from ideality. (½)

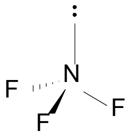
(b) Explanation in terms of dimer formation via hydrogen bonding. (1) Structure of dimer with molar mass 60 (rmm of monomer) X 2 = 120 which is found at low temperatures when it can survive dissociation.



(1)

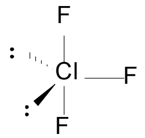
At high temperature, dimer dissociates fully into monomer and the molecular weight changes to 60. (1) At intermediate temperatures, the rmm is the weighted average of 60 and 120, depending on the degree of dissociation at that temperature. (2)

(c) Explanation in terms of the VSEPR theory of electron repulsion including BP-BP < BP-LP < LP-LP (1): in BF3, 3 BPs surrounding central B atom hence a trigonal planar structure (1) ; in NF_3 3 BPs and one LP on N, hence shape is trigonal pyramidal due to the LP spatial requirement with FNF angle smaller than 109.5^{o}:



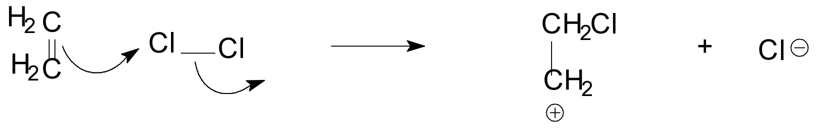
(1)

In ClF_3, there are 2 LP and 3 BP surrounding the Cl (1) ; the 2 LPs are accommodated in the equatorial plane of a trigonal bipyramidal distribution of electron pairs so that chlorine trichloride assumes a planar T-shape [the F-Cl-F (axial F's) angle is smaller than 180^{o}: do not penalize if this feature if not mentioned]



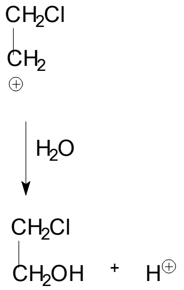
(1)

(d) Formation of carbocation explained as a result of electrophilic addition of Cl_2 molecule on double bond: (1)



(1)

Formation of 1,2-dichloroethane occurs in a second step resulting from addition of chloride ion (1) ; but if the carbocation is attacked by water, also a nucleophile , (1) the product, after deprotonation following initial addition, will be 2-chloroethan-1-ol:

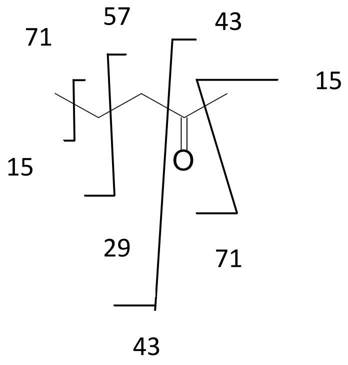


(1)

(e) The peak at m/z 86 represents the parent peak (molecular ion) and this does not help distinguish between the two isomers (½).

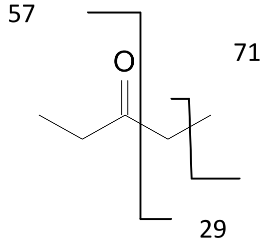
The two ketones are expected to produce fragmentation peaks by breakage of C-C bonds which are weaker than C=O bond (½) as follows:

Pentan-2-one to form fragments at m/z 71, 43, 29, 15 as shown:



(1)

Pentan-3-one to form fragments at m/z 71, 57, 29 and 15 as shown (NB molecule has plane of symmetry through the carbonyl group).



(1)

The fact that m/z 71 and m/z 15, both possible from <u>both</u> ketones are, in fact, not observed as main peaks in the mass spectrum of the unknown suggests that <u>cleavage does not occur equally readily at all possible C-C bonds.</u> (½) Clearly, the two peaks at m/z 57 and 29 both result from cleavage of a particular bond that is favoured: in pentan-3-one, such a bond is the one that is next (alpha) to the C=O. There are two corresponding bonds in pentan-2-one: one of them (C_2-C_3) would give a single peak at m/z 43 due to fragments $C_3H_7^+$ and CH_3CO^+; the other bond (C_1-C_2) would form two peaks, one at m/z 71 due to $C_3H_7CO^+$ and another at m/z 15 due to CH_3^+. (½) Lack of m/z 43 among the <u>main fragmentation</u> peaks observed (29 and 57) must imply that the ketone in question is pentan-3-one. (1)

Give credit to other reasonable answers, 1 for the correct identity of the ketone and 4 for the reasons given at arriving at the answer.

6. Explain the following statements using chemical principles and facts. Provide chemical equations where necessary.

(a) Sodium hydrogencarbonate (baking soda) and ammonium hydrogencarbonate are leavening agents: food additives that produce bubbles in dough or batter, causing baked goods to rise. The leavening effect from a given mass of ammonium hydrogencarbonate is better than that from the same mass of sodium hydrogencarbonate, however the ammonium salt is best used in making flat cookies and pastries but not for baking large cakes. *(4 marks)*

(b) The colour of the flower of the hydrangea is known to depend on the soil pH. Periodic treatment of the soil with aluminium sulfate results in blue hydrangeas. *(3 marks)*

(c) When zinc granules were added to a solution of potassium dichromate(VI) in dilute sulfuric acid, the orange solution turned green. When the reaction was repeated in the absence of air, the green solution finally turned sky-blue but the solution became green again when shaken with air. When a solution of potassium dichromate(VI) is treated with alkali, the orange solution turns yellow. *(5 marks)*

(d) Copper(II) chloride dissolves in water to give a blue solution. When concentrated hydrochloric acid is added, the solution turns green. *(3 marks)*

(e) Magnesium sulfate is more soluble than barium sulfate but barium hydroxide is more soluble than magnesium hydroxide.

(5 marks)

(a)

Both sodium hydrogencarbonate and ammonium hydrogencarbonate decompose on heating at relatively low temperatures to liberate gaseous products. ½

On heating:
$NH_4HCO_3 \rightarrow NH_3 + H_2O + CO_2$ ½
$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$ ½
Accept also reaction of bicarbonate with acid

NH_4HCO_3 is a better leavening agent than $NaHCO_3$ because it gives more gas bubbles for the same amount in grammes of powder: ½

1 mole NH_4HCO_3 (79g) produces 2 moles of gas ½

$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$
2 moles $NaHCO_3$ (168g) produces one mole of gas ½

Ammonium bicarbonate can only be used to make flat cookies and pastries that are small enough to allow the ammonia odour to dissipate while baking. Otherwise the unpleasant ammonia taste will remain in the cake. 1

(b)

The charge/radius ratio of Al^{3+} is very high 1
This makes aluminium salts acidic in solution:
$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(OH)(H_2O)_5]^{2+} + H_3O^+$ 1
Aluminium sulfate renders the soil acidic ½
Therefore hydrangeas are blue in acidic soil ½

(c)

Zinc in acid reduces orange potassium dichromate (VI) to green Cr^{3+} (in the presence of air) ½

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2\,Cr^{3+} + 7H_2O$ 1

Zinc in acid reduces orange potassium dichromate (VI) to sky-blue Cr^{2+} (in the absence of air) ½

$Cr_2O_7^{2-} + 14H^+ + 8e^- \longrightarrow 2Cr^{2+} + 7H_2O$ 1

When shaken in air Cr^{2+} is oxidised to Cr^{3+}

$Cr^2 \longrightarrow Cr^{3+} + e^-$ ½

½

Orange potassium dichromate is turned to yellow potassium chromate(VI) in the presence of alkali

½

$Cr_2O_7^{2-} + 2OH^- \longrightarrow 2CrO_4^{2-} + H_2O$

½

(d) The blue solution is due to $[Cu(H_2O)_4]^{2+}$ or aquated copper(II) ion (accept as correct if shown as hexaaquacopper(II)) 1

On adding concentrated hydrochloric acid, <u>ligand replacement</u> occurs giving rise to a green solution containing $[CuCl_4]^{2-}$ (1). 1

(e)

The sulfate ion is a large ion; magnesium sulfate and barium sulfate have comparable lattice enthalpies. 1

However the hydration enthalpy of the Mg^{2+} ion is much larger than the hydration enthalpy of Ba^{2+} due to the small size of Mg^{2+}. 1

Thus magnesium sulfate is soluble while barium sulfate is not.

The hydroxide ion is a small ion. This results in a high lattice enthalpy in magnesium hydroxide due to small ions present. 1

The lattice enthalpy of barium hydroxide is not large due to the large barium ion. 1

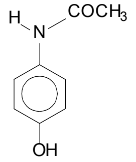
The low lattice enthalpy outweighs the decrease in the enthalpy of hydration from Mg to Ba, hence the solubility of barium hydroxide is greater than that of magnesium hydroxide. 1

7. (a) Explain with reasons which of the following species can function as an electrophile, as nucleophile and which has neither function:

NH_3; CH_3^-; NH_2^-; Br^+; CH_3OH; CH_4; $C_6H_5CH_2^+$; NH_4^+

(7 marks)

(b) When 4-aminophenol is treated with ethanoic anhydride, the following product is formed.



Identify the electrophile which is formed from ethanoic anhydride and explain why this species forms a bond with the nitrogen rather than the more electronegative oxygen atom in the aminophenol.

(3 marks)

(c) Alcohols react with carboxylic acids to form esters but phenols require treatment with carboxylic acid derivatives. *(4 marks)*

(d) Benzoic acid is purified by recrystallisation from water. Write a procedure for carrying out this operation on about 5 g crystals of this acid which a student of chemistry could follow. Briefly explain the principle of this purification technique and also explain how the student could check the purity of the recrystallised acid.

(6 marks)

(a) NH_3; CH_3^-; NH_2^-; CH_3OH; (½ ½ ½ ½) act as nucleophiles, due to presence of lone pair; negative charge makes nucleophiles stronger. (½,½)

Br^+; $C_6H_5CH_2^+$ (½ ½) act as electrophiles and accept electron pairs to form covalent bonds with positively charged atoms (½ ½)

CH_4; NH_4^+ (½ ½) have no electron pair (½) nor can form additional bonds with electron pair donors (½) hence are neither nucleophiles nor electrophiles.

(b) Electrophile is CH_3CO^+ (1)

The amide product forms as a result of covalent bond formation by the lone pair on the N (or O) atom and the carbon of the ethanoyl cation (½).

Since N is less electronegative than O, the electron pair on N is less tightly held to the atom than the electron pair on O and hence it is more readily donated to the ethanoyl cation so that the nitrogen substituted product forms. (1 ½)

(c) Reaction occurs as a result of nucleophilic attack by ROH on the $\partial +$ charge of the carbonyl oxygen in COOH group. (1) In phenols, the lone pair on the OH group is delocalized onto the benzene ring (½) and is less available for donation to carbonyl carbon (½) ;

in the carboxylic acid derivatives, namely, acid chlorides and acid anhydrides (½ ½) the partial positive charge on the carbonyl carbon is enhanced by inductive effect of the electronegative Cl/O linked to CH_3- C=O group (½) so that even weak nucleophiles such as phenols can bond successfully with the carbonyl carbon atom (½).

(d) The crystals are dissolved in the minimum amount of nearly boiling water (1), the hot solution is filtered to remove any insoluble impurities (½) and the filtrate is allowed to cool when it deposits recrystallised purer benzoic acid. Soluble impurities are left behind in the solution. (½) The recrystallised acid is filtered and washed with more distilled water to remove traces of the mother liquor (½ ½).

Principle of method: since solubility increases with temperature, benzoic acid and its impurities dissolve in hot water to a greater extent than in cold. (1) Hence the reprecipitated crystals obtained on cooling would contain less impurities which remain dissolved or are filtered if insoluble prior to recrystallisation. (1)

Taking the melting point of the dried crystals would serve as a criterion of purity. (1)

8. Give a practical laboratory method of preparation for small amounts of each of the following substances starting from the indicated substance and using other readily available materials and including essential details. In your account, include balanced chemical equations for the reactions mentioned. More than one step may be required in certain cases. For (c) and (d), assume deuterium oxide is available. Each section carries equal marks.

(a) anhydrous iron(II) chloride from iron;
(b) sodium thiosulfate-5-water from sodium sulfite;
(c) dideuteroethyne (C_2D_2) from carbon;
(d) lithium tetradeuteridoaluminate ($LiAlD_4$) from lithium and aluminium;
(e) potassium manganate(VI) from manganese(IV) oxide. *(20 marks)*

(a) $FeCl_2$: Pass dry HCl gas over iron filings heated in a tube. (2)

$Fe + HCl = FeCl_2 + H_2$ (1)

The HCl could be made by heating a mixture of NaCl and concentrated sulfuric acid. (½)

$NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl$ (½)

Award no marks if method involves adding Fe to dilute HCl and then drying crystals.

(b) Dissolve elemental sulfur in hot sodium sulfite solution (1) followed by filtration of unreacted sulfur and crystallization of the solution (1)

$Na_2SO_3(aq) + S\,(s) = Na_2S_2O_3\,(aq)$

$Na_2S_2O_3\,(aq) + 5\,H_2O\,(l) = Na_2S_2O_3.5\,H_2O\,(s)$ (1, 1)

(c) Calcium oxide is heated strongly with C (1)

$CaO\,(s) + 3\,C(s) = CaC_2\,(s) + CO\,(g)$ (1)

Then, calcium carbide is treated with deuterium oxide to produce dideuteroethyne: (1)

$CaC_2\,(s) + 2\,D_2O\,(l) = C_2D_2\,(g) + Ca(OD)_2\,(s)$ (1)

(d) Lithium is treated with deuterium gas obtained from D_2O by electrolysis or by reaction with lithium metal: $2\,Li(s) + D_2\,(g) = LiD\,(s)$ (1)

Al is treated with dry chlorine gas: $Al\,(s) + 3/2\,Cl_2\,(g) = AlCl_3\,(s)$ (1)

The products are mixed in ether as solvent, the LiCl precipitate is filtered off and the lithium tetradeuteroaluminate is obtained by crystallisation from ether: (1)

$AlCl_3$ (ether) + $LiD\,(s)$ = $LiAlD_4$(ether) + $LiCl(s)$ (1)

(e) The oxide is heated with KOH in presence of air or oxygen: (1)

$2\,MnO_2 + 4\,KOH + O_2 \rightarrow 2\,K_2MnO_4 + 2\,H_2O$ (2)

The green solution is separated from unreacted solids and purified by recrystallization. (1).

Accept other reasonable answers for all the above conversions.

Paper 3

1. (b) 25.00 cm^3 **F** (ammonium iron(II) sulfate) reacts with solution $\mathbf{P_n}$ (MnO_4^-) as follows:

28.95 cm^3 **(odd)**

23.08 cm^3 (**even**)

Award for true value ± 0.10 mL = **25 marks**

± 0.15 mL = 15 marks

± 0.20 mL = 10 marks

The 'true value' should correspond with two or more actual experimental titre values shown in the table to be concordant. If the student takes the average of all titre values, including overshot (rough) titres, and obtains a bad average titre value as a result, deduct 5 marks from the score as merited according to the above scheme. Conversely, if the average value is indeed equal to the true value *but no two experimental titre values agree to ± 0.1 with the true value*, then award ONLY 5 marks.

(d) For correct calculation of the molar concentration of potassium permanganate solution in $\mathbf{P_n}$ **award 5 marks.**

(f) 25.00 cm^3 $\mathbf{P_n}$ (ammonium iron(II) sulfate) reacts with solution **H** (H_2O_2) as follows:

9.10 cm^3 **(odd)**

11.40 cm^3 (**even**)

Except that for the following candidate office numbers 349 to 378 and 437, 438 and 444, the true titre values in (f) are as follows:

8.93 cm^3 **(odd)**

11.20 cm^3 **(even)**

Award for true value ± 0.10 mL = **15 marks**

± 0.15 mL = 10 marks

± 0.20 mL = 5 marks

The 'true value' should correspond with two or more actual experimental titre values shown in the table to be concordant. If the student takes the average of all titre values, including

overshot (rough) titres, and obtains a bad average titre value as a result, deduct 5 marks from the score as merited according to the above scheme. Conversely, if the average value is indeed equal to the true value *but no two experimental titre values agree to ± 0.1 with the true value*, then award ONLY 5 marks.

(g) For the correct calculation of the molar concentration of hydrogen peroxide in solution **H** **award 5 marks.**

(50 marks)

2. You are provided with an aqueous solution of an inorganic substance labelled **V** which is a double salt containing a common ion. Carry out the following tests on about 1 cm^3 samples of the solution and record your observations and inferences in the spaces provided.

(a) Add dilute sodium hydroxide dropwise until in excess. Heat the mixture to boiling (CARE! Sodium hydroxide is caustic) and test for any gases evolved.

Observation	*Inference*
White gelatinous precipitate forms which is soluble in excess NaOH to give a colourless solution. On heating solution, a colourless gas with a sharp odour which turns litmus blue is released **(4)** [NB Prolonged heating may cause reformation of the white precipitate. This is possibly due to reaction of ammonium ion with zincate ion: $Zn(OH)_4^{2-} + 2\ NH_4^+ = Zn(OH)_2 + 2\ NH_3 + H_2O$] **If this observation is reported give a bonus of 1 mark, whether accompanied by an explanation or not. If a correct explanation is also given, award another bonus of 1 mark.**	The white precipitate could be a hydroxide of Al, Zn, Pb which redissolves as it forms the metallate ion, e.g. $Zn(OH)_4^{2-}$ or $Al(OH)_4^-$. **(2)** Ammonium ion is also present to explain the release of ammonia from the solution on heating. $NH_4^+ + OH^- = NH_3 + H_2O$ **(2)**

(b) Add aqueous ammonia dropwise until in excess.

Observation	*Inference*
White gelatinous precipitate forms which is soluble in excess ammonia to give a colourless solution. **(3)**	This suggests that the metal cation is Zn not Al or Pb because $Zn(OH)_2$ which forms when hydroxide ion is added dissolves in presence of excess NH_3 to form $Zn(NH_3)_4^{2+}$ **(3)**

(c) Add drops of sodium carbonate solution.

Observation	*Inference*
White precipitate forms. **(2)**	Zinc carbonate forms as an insoluble white precipitate. **(2)**

(d) Add two drops of dilute nitric acid followed by 5 drops of silver nitrate solution and then add dilute aqueous ammonia until in excess.

Observation	*Inference*
White precipitate forms which is soluble in dilute ammonia to give a colourless solution. **(3)**	Chloride is present: AgCl forms which dissolves in ammonia forming $Ag(NH_3)_2^{+}$. **(2)**

Conclusion:

V is probably a solution of the double salt: ammonium zinc chloride **(2)**

(25 marks)

3. You are provided with an organic solid substance **S** having more than one functional group**.** Perform the following tests on **S** and record your observations and inferences in the spaces provided.

(a) Burn about 0.2 g of **S** on a crucible lid. Do not allow the flame to burn longer than you need to make a good observation.

Observation	*Inference*
Compound melts and then ignites with	Probably an aromatic or highly

difficulty to give a smoky luminous flame. **(2)**	unsaturated compound. **(2)**

(b) Shake a few crystals of **S** with about 1 cm^3 water and warm the mixture; test the pH of the solution with litmus paper. *Keep mixture for test (c).*

Observation	*Inference*
Compound is insoluble/slightly soluble in cold water but dissolves better on gentle heating; blue litmus turns pinkish. **(2)**	Possibly an acidic group is present, either carboxylic or phenol. **(2)**

(c) To part of the product from test (b), add drops of bromine water.

Observation	*Inference*
Bromine water was decolorized and a white precipitate formed. **(2)**	Confirms presence of a phenol. The ppt is probably a tribromophenol. Also S is aromatic not unsaturated aliphatic hydrocarbon. **(2)**

(d) To product in test (b), add drops of neutral iron(III) chloride solution.

Observation	*Inference*
A violet-blue (purple) colour forms. **(2)**	Confirms presence of a phenol. **(2)**

(e) Add a few crystals of **S** to aqueous sodium carbonate.

Observation	*Inference*
Effervescence was observed and a colourless odourless gas was given off that turned lime water milky. **(2)**	Indicates presence of a carboxylic acid which, unlike phenol, liberates carbon dioxide from carbonates. **(2)**

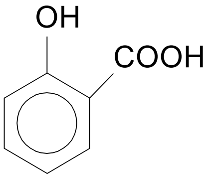
(f) To about 0.3 g **S** add about 3 cm^3 of propan-1-ol, one drop of concentrated sulfuric acid (CARE! CORROSIVE) and heat the mixture in a boiling water bath for a few minutes. Tip the products of this reaction in a solution of sodium carbonate.

Observation *Inference*

On adding mixture to sodium carbonate solution, effervescence observed and a clear upper layer formed. Odour similar to that of oil of wintergreen evolved. **(2)**	Probably, the reaction mixture contained an ester formed by reaction between the carboxylic acid group in S and propan-1-ol. **(2)**

Conclusion:

Substance **S** is possibly:



(or isomer, or homologue: provided the given structure has (an aromatic ring; a phenol; a carboxylic acid) [1]

(25 marks)